

X-Ray Diffraction and EXAFS Analysis of Materials for Lithium-Based Rechargeable Batteries

M. D. Sharkov^a, M. E. Boiko^a, A. V. Bobyl^a, E. M. Ershenko^a, E. I. Terukov^a,
and Y. V. Zubavichus^b

^a Ioffe Physical-Technical Institute, Russian Academy of Sciences,
ul. Politekhnicheskaya 26, St. Petersburg, 194021 Russia

e-mail: mischar@mail.ioffe.ru

^b National Research Centre “Kurchatov Institute”, pl. Kurchatova 1, Moscow, 123182 Russia

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Abstract—Lithium iron phosphate LiFePO_4 (triphylite) and lithium titanate $\text{Li}_4\text{Ti}_5\text{O}_{12}$ are used as components of a number of active materials in modern rechargeable batteries. Samples of these materials are studied by X-ray diffraction and extended X-ray absorption fine structure (EXAFS) spectroscopy. Hypotheses about the phase composition of the analyzed samples are formulated.

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INTRODUCTION

Compounds such as lithium iron phosphate LiFePO_4 (known also under the name triphylite) and lithium titanate $\text{Li}_4\text{Ti}_5\text{O}_{12}$ are active materials used in modern rechargeable batteries. It is known that these compounds prepared by chemical methods can contain foreign phases which can differ in the size, shape, and even physical state. Hence, samples of triphylite or lithium titanate may be composed of either perfect crystalline or amorphous grains. Such samples can be successfully studied by combined methods. First, the atomic structure was investigated by extended X-ray absorption fine structure (EXAFS) spectroscopy, which is sensitive to materials in any physical state. Second, the structure of the crystalline components of the sample was studied by X-ray diffraction.

EXPERIMENTAL DATA MEASUREMENTS

Two samples of triphylite and one sample of lithium titanate were prepared by chemical etching in the St. Petersburg State Technological Institute (Technical University). The EXAFS spectra of all samples (at the Ti K-edge for titanate and at the Fe K-edge for phosphate) were measured at the Structural Materials Science beamline on the SIBIR-2 synchrotron radiation source at the National Research Centre “Kurchatov Institute” (NRC KI). The measurements were performed in the reflection mode using two ionization chambers filled with $\text{N}_2\text{—Ar}$ gas mixtures. The energy was scanned using a Si(111) channel-cut monochromator. For one of the samples (sample 1), the EXAFS spectrum was repeatedly recorded 3 months after the first spectrum. One EXAFS spectrum was measured for another triphylite sample (sample 2).

The Fe K-EXAFS spectra recorded for both samples of LiFePO_4 are shown in Fig. 1. Figure 2 displays the EXAFS spectrum at the Ti K-edge for the titanate sample.

Both triphylite samples were studied also by X-ray diffraction. Figure 3 shows the X-ray diffraction (XRD) data for lithium iron phosphate samples 1 and 2, respectively.

The X-ray diffraction data were collected on a Bruker D8-DISCOVER instrument in the Ioffe Physical-Technical Institute of the Russian Academy of Sciences using monochromated $\text{Cu}-K_\alpha$ beams (the

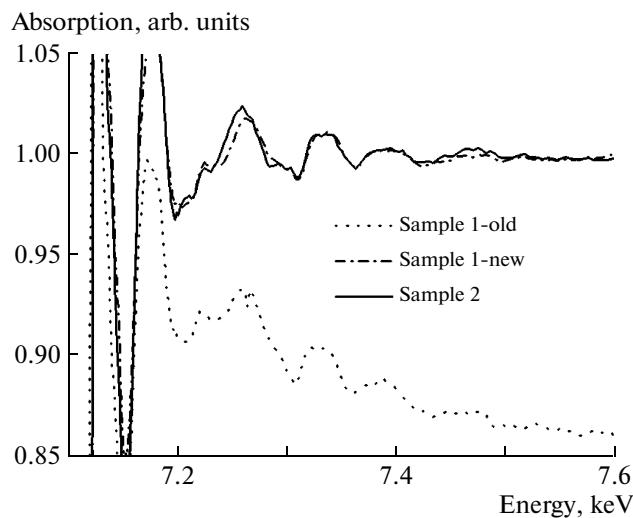


Fig. 1. The Fe K-EXAFS spectra for two samples of LiFePO_4 .

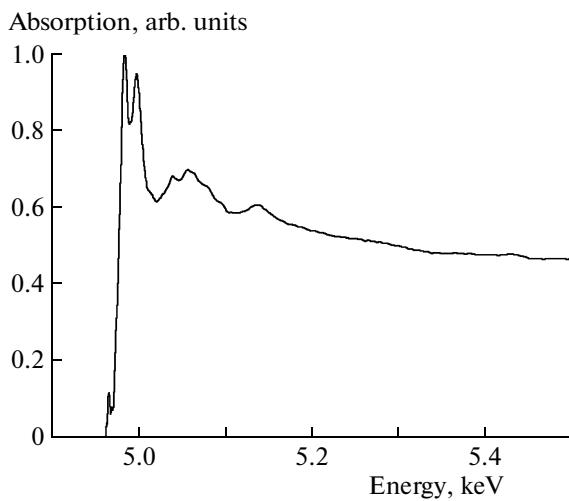


Fig. 2. The Ti K-EXAFS spectrum for the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ sample.

wavelength was 1.54 \AA) and a four-crystal Ge(220) channel-cut monochromator.

The X-ray diffraction curves have a definite saw-tooth shape characteristic of two-dimensional structures (graphene, adsorbates, carbon nanotubes, films composed of several atomic layers, and so on). In addition, the diffraction peaks for both samples were much broader than the standard empirical XRD peaks. This situation is typical of powder and dispersed media.

It has been found that the sample 1 has a considerable magnetic moment. This fact suggests that the sample contains ferromagnetic impurity phases. The data presented in Fig. 3 provide evidence that the sample 1 can contain a phase component with the spinel-lattice structure [2], whereas the presence of a considerable spinel fraction in the sample 2 is unlikely. Unfortunately, the X-ray diffraction data did not allow

us to precisely determine the fraction of a particular spinel material in sample 1 (although a spinel compound can attach ferromagnetic properties to the sample).

PROCESSING EXAFS DATA

All EXAFS spectra under consideration were processed according to a new method which we developed earlier [3]. This method implements the separation of oscillations of the spectrum based on the variational principle and the rough estimation of the boundaries of the Fourier-transform window, which, nevertheless, makes it possible to reduce the effect of the experimental noise on the results of an analysis of the spectrum.

To separate the oscillating part from the EXAFS spectrum under consideration, a special functional was constructed. This functional should take the minimum value for the sought smooth part of the spectrum required for the calculation of oscillations. The functional consists of integral terms, which are responsible for the smoothness of the sought function, its resemblance to the spectrum, and the fact that the integral of the difference between the spectrum and its smooth part over the range of processing is equal to zero. The problem of the functional minimization can be transformed to the Euler–Lagrange equation taking the following form:

$$\left(\frac{d^2}{dE^2} - C^2 \right) \mu_0 = C^2 (4A - \mu),$$

where E is the energy of photons, μ is the EXAFS spectrum with the smooth component μ_0 , and A and C are the parameters of processing related to each other by the condition that the integral of the function $\mu(E) - \mu_0(E)$ is equal to zero. The addition of two first-kind boundary conditions causes this problem to be unambiguous. The optimal value of C should be

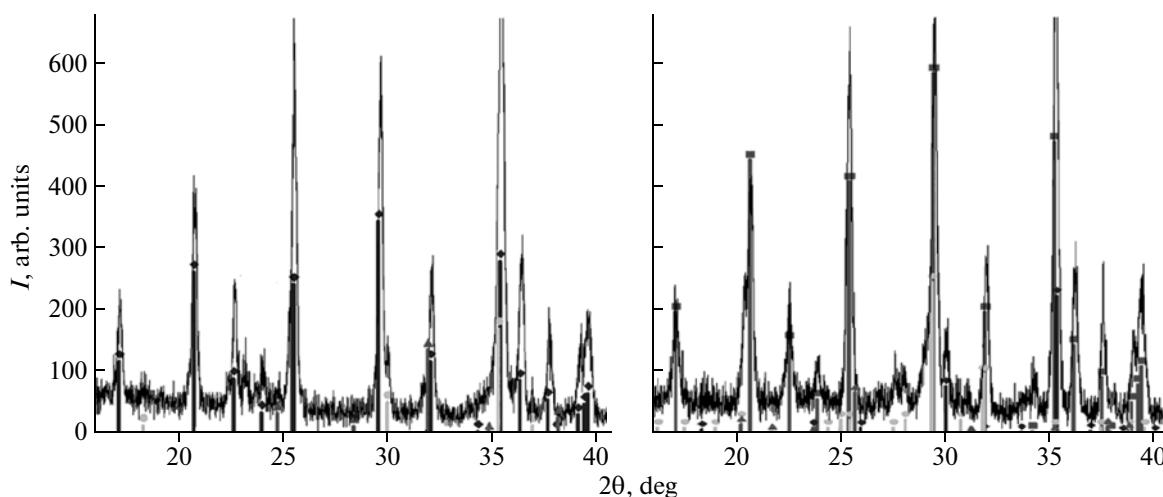


Fig. 3. XRD data for the LiFePO_4 samples: 1 (on the left) and 2 (on the right).

taken approximately as the inverse period of oscillations of the spectrum μ [4].

The dependence of the EXAFS-spectrum analysis results on the positions of the Fourier-transform window boundaries was studied for a series of the spectra of metals (V, Cr, Co, Cu, Zr, and Ag) [4]. It appeared that the most correct results of the EXAFS data processing can be obtained when the position of the lower boundary of the Fourier-transform window is 40 to 80 eV higher than the absorption edge and the window width is between 300 and 600 eV. Wider windows lead to a more substantial contribution of the noise to the Fourier transform of oscillations.

Procedures which would allow one to automatically determine the optimal boundaries of the Fourier-transform window of EXAFS from the spectral pattern are being lacked.

RESULTS AND DISCUSSION

Figures 4 and 5 display the Fourier transforms of the EXAFS spectra at the Ti K-edge for LiFePO_4 and at the Fe K-edge for $\text{Li}_4\text{Ti}_5\text{O}_{12}$, respectively.

The spectrum of lithium titanate was converted to the curve of the pseudodensity distribution of interatomic distances as follows. The energy of the edge was determined from the position of the maximum of the first derivative of the spectrum with respect to the energy $d\mu/dhv$. This commonly used method [1, 5] gave the value of the edge equal to 4.977 keV. The oscillations of the spectrum were separated according to a method based on the above-described variational principle. The smooth part was determined in the range from 5.030 to 5.500 keV. The following parameters of the processing were chosen: $C = 50 \text{ keV}^{-1}$ and $A = -0.02$. The Fourier transform of the spectrum was performed in the range from 5.030 to 5.400 keV with

the weight function k^2 . Figure 4 displays the Fourier transform of the spectrum of the titanate. Figure 4 also shows the Fourier transforms of the Ti K-EXAFS spectra for titanium dioxide TiO_2 in the anatase phase (like the spectrum of the sample under study, this EXAFS spectrum was measured on the synchrotron radiation source at NRC KI) and relatively pure lithium titanate $\text{Li}_4\text{Ti}_5\text{O}_{12}$ [6]. These Fourier transforms are also shown in Fig. 4.

When the amplitudes of EXAFS oscillations are much smaller in magnitude than unity, the oscillations of the spectrum can be approximately described as a linear combination of the spectra of different phase components of the sample. Therefore, a certain criterion for estimating the phase composition of the sample can be obtained. The minimum value of the integral, which depends on the Fourier transforms of the spectra of the sample χ and its assumed components χ_j , can serve as this criterion:

$$\int_{R_1}^{R_2} \left(\tilde{\chi}(R) - \sum_j \alpha_j \tilde{\chi}_j(R) \right)^2 dR,$$

where α_j is a coefficient which is approximately proportional to the volume fraction of the absorbing atoms within the corresponding sought component of the sample. These values are, apparently, related to the volume fractions of the phase components of the sample. In this case, the limits of integration R_1 and R_2 were taken equal to 1 and 4 Å, respectively. This choice was determined by the following reasons. First, the Fourier transform of EXAFS for interatomic distances smaller than 1 Å is formed mainly due to experimental errors and errors of the processing rather than by the real coordination spheres. Second, at distances larger

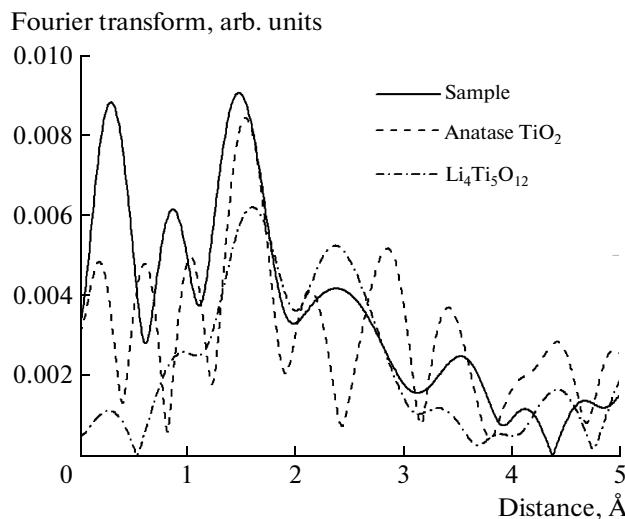


Fig. 4. Fourier-transformed EXAFS spectra for the lithium titanate sample and two reference materials.

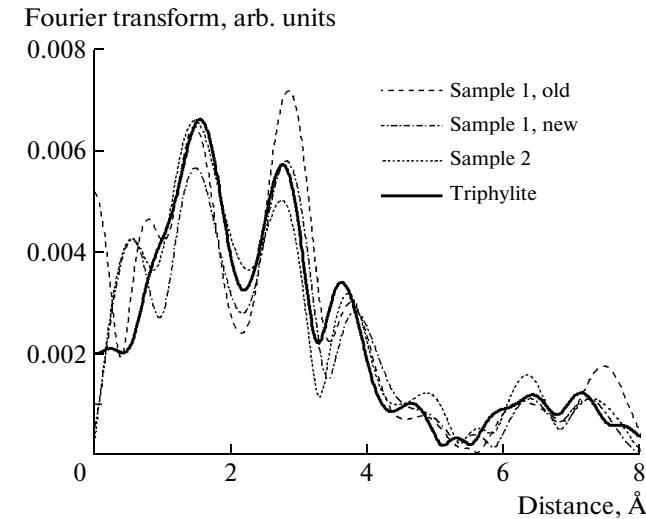


Fig. 5. Fourier-transformed EXAFS spectra for LiFePO_4 from the experimental results and literature data [7].

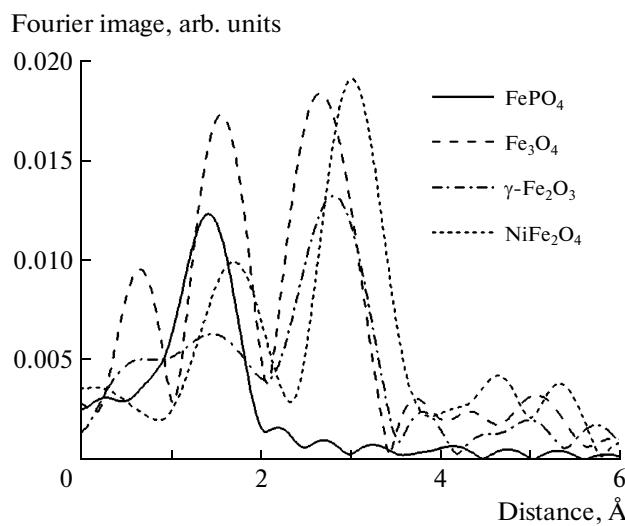


Fig. 6. Fourier-transformed EXAFS spectra at the Fe K-edge for references materials (Fe_3O_4 , $\gamma\text{-Fe}_2\text{O}_3$, FePO_4 , and NiFe_2O_4) that are presumably present in both LiFePO_4 samples.

than 4 Å, the Fourier transforms of oscillations are much weaker than the nearest coordination spheres.

This approach was applied to the experimental and reference spectra under consideration. It was shown that the volume fractions of the titanate and anatase in the sample may account for 60 and 40%, respectively. Therefore, it can be suggested that the sample consists of similar volumes of the phase components $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and TiO_2 in the anatase form.

All three spectra of triphylite were analyzed by analogy with the EXAFS spectrum of titanate. Initially, the limiting value of the energy was determined from the maximum of the first derivative for each EXAFS curve under consideration. These values are 7.118 keV for the early spectrum of sample 1 and 7.121 keV for the other two spectra. To separate oscillations, each spectrum was processed as described above. The parameters of the processing are as follows: $C = 20 \text{ keV}^{-1}$ and $A = -0.6$ in the energy range from 7.165 to 7.500 keV for the spectrum of sample 1 measured earlier; $C = 18 \text{ keV}^{-1}$ and $A = -0.35$ in the energy range from 7.192 to 7.500 keV for the spectrum of sample 1 measured later; $C = 18 \text{ keV}^{-1}$ and $A = -0.45$ in the energy range from 7.161 to 7.500 keV for the spectrum of sample 2.

To estimate the phase composition of both samples of the phosphate, we used the reference EXAFS data for several Fe-containing substances. These are triphylite by itself (the spectrum was taken from [7] and is shown in Fig. 5), magnetite Fe_3O_4 , maghemite $\gamma\text{-Fe}_2\text{O}_3$ (both spectra were taken from [8]), nickel ferrite (nickel iron oxide) NiFe_2O_4 (the spectrum was taken from [9]), and iron-III phosphate FePO_4 (the spec-

trum was taken from [7]). The Fourier transforms of these spectra are shown in Fig. 6.

These data were processed according to the same procedure as was applied to the spectrum of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ sample. The following estimates of the volume fractions were obtained. In the first measurement, the sample 1 was, apparently, composed of approximately 85% of lithium iron phosphate, about 10% of maghemite, and a few percentage of both FePO_4 and NiFe_2O_4 . In the second measurement, sample 1 apparently contained only about 1% maghemite (in addition to triphylite). The sample 2 probably consisted of 90–95% triphylite and 5–10% iron phosphate. The presence of maghemite phases is unlikely in both samples. Therefore, it was shown that the sample 2 initially contained smaller amounts of foreign components compared to the sample 1. However, at the moment of the measurement of the second spectrum, the composition of the sample 1 was more similar to pure triphylite when compared to the sample 2 at the moment of the measurement of the EXAFS spectrum.

CONCLUSIONS

The XRD and EXAFS analysis of a sample of lithium titanate at the Ti K-edge using the method of processing spectra that we developed earlier showed that the sample apparently contains a TiO_2 component in the anatase phase, whose volume fraction accounts for approximately one-half of the sample.

The analysis of the XRD data and EXAFS spectra at the Fe K-edge for riphylite samples showed that the sample 1 probably contains, in addition to triphylite, approximately 10% maghemite $\gamma\text{-Fe}_2\text{O}_3$ and a few percentages of both FePO_4 and NiFe_2O_4 at the moment at which the first spectrum is measured. The same sample apparently contains triphylite and about 1% maghemite (volume fraction) at the moment at which the second spectrum is measured. It was also shown that the sample 2 is probably composed of 90–95% triphylite and 5–10% FePO_4 .

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